

PTO 07-4619

CC = JP
20010703
Kokai
13181035

PIEZOELECTRIC CERAMIC COMPOSITION
[Atsudenseramikkusoseibutsu]

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JUNE 2007
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY (19): JP

DOCUMENT NUMBER (11): 13181035

DOCUMENT KIND (12): Kokai

PUBLICATION DATE (43): 20010703

APPLICATION NUMBER (21): 11372987

APPLICATION DATE (22): 19991228

INTERNATIONAL CLASSIFICATION⁷ (51): C 04 B 35/49, 35/495, H 01 L 41/187

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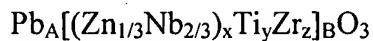
APPLICANT (71): TDK Corp.

TITLE (54): PIEZOELECTRIC CERAMIC COMPOSITION

FOREIGN TITLE [54A]: Atsudenseramikkusoseibutsu

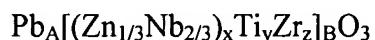
Claims

1. Piezoelectric ceramic composition comprising oxide composition of basic composition formula:



[In the formula, A, B, x, y and z are atomic ratios satisfying the following conditions: $0.96 \leq A/B < 1$; $x + y + z = 1$; $0.05 \leq x \leq 0.40$; $0.1 \leq y \leq 0.5$; $0.2 \leq z \leq 0.6$]

2. Piezoelectric ceramic composition comprising oxide composition of basic composition formula:



[In the formula, A, B, x, y and z are atomic ratios satisfying the following conditions: $0.96 \leq A/B < 1$; $x + y + z = 1$; $0.05 \leq x \leq 0.40$; $0.1 \leq y \leq 0.5$; $0.2 \leq z \leq 0.6$] with addition of more than 0.2 wt% but less than 1.0 wt% of at least one oxide chosen from Ta_2O_5 , Sb_2O_3 and Nb_2O_5 .

Detailed explanation of the invention

[0001]

Technological field of the invention

The present invention concerns piezoelectric ceramic compositions used in piezoelectric vibrators such as piezoelectric sound generators, piezoelectric actuators, etc., especially concerns piezoelectric ceramic compositions containing $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 - PbZrO_3 as main component.

[0002]

Conventional technology

Conventionally, ternary piezoelectric ceramics of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 - PbZrO_3 have been known (Japanese Kokoku Patent No. Sho 44[1969]-17344). Other piezoelectric ceramics known are such

ternary piezoelectric ceramics of which a portion of lead atom is replaced by calcium, strontium or barium for enhanced dielectric constant (Japanese Kokoku Patent No. Sho 45[1970]-39977). In Japanese Kokai Patent No. Sho 61[1986]-129888, for enhanced specific dielectric constant and electromechanical bonding coefficient, a portion of lead atom in the similar ternary piezoelectric ceramics is replaced by Ba and Sr. In Japanese Kokai Patent No. Hei 03[1991]-256379, contents of Pb, Ba and Sr in such piezoelectric ceramics are limited to certain ranges for solving problems of performance variations among products and for enhanced piezoelectric constant.

[0003]

Problems to be solved by the invention

Piezoelectric ceramics have been used widely in piezoelectric filters, piezoelectric transformers, ultrasonic vibrators, piezoelectric sound generators, piezoelectric actuators, piezoelectric buzzers, etc. Of these, recently, size reduction and thickness reduction are attempted for piezoelectric vibrators such as piezoelectric sound generators, piezoelectric actuators, etc. Especially, piezoelectric actuators are noted for application, e.g., as micro actuators for hard disk drive head for personal computers, and with enhanced recording density, development of ultra-micro piezoelectric actuators capable of controlling micro displacement in submicron order is carried out. Especially for displacement control actuators, piezoelectric materials should have excellent piezoelectric properties, i.e., high piezoelectric constant d. In general, piezoelectric constant d, electromechanical bonding coefficient k and specific dielectric constant ϵ have a relationship of $d \propto k\sqrt{\epsilon}$. Thus, for increasing the piezoelectric constant d, the electromechanical bonding coefficient k and specific dielectric constant d have to be increased. With reduction in size and thickness, the piezoelectric devices have reduced mechanical strength and increased possibility of damage during production process and device operation, leading to reduced

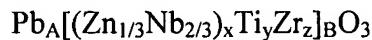
product yield and performance reliability. Thus, piezoelectric ceramic compositions of good mechanical strength are desired, and development of lamination-type piezoelectric devices is carried out.

Conventional ternary piezoelectric ceramics of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 - PbZrO_3 have a high sintering temperature of about 1200°C. Thus, in making laminated piezoelectric devices from such piezoelectric ceramic compositions, very expensive noble metals such as platinum or palladium that withstand such high sintering temperature have to be used for inner electrodes, leading to problems of high production cost. If the sintering temperature can be lowered, less expensive silver-palladium alloys can be used for inner electrodes. When silver-palladium alloys are used for the inner electrodes, with high content of expensive palladium, redox reaction of palladium occurs during sintering, leading to cracking or peeling in the laminated piezoelectric devices, thus the palladium content should be kept below 30%. With palladium content below 30%, according to the Ag-Pd phase diagram, the sintering temperature should be below 1150°C, preferably below 1120°C. Thus, when conventional ceramic compositions of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 - PbZrO_3 are used for making lamination type piezoelectric devices, making fine powder or HIP treatment is necessary. Furthermore, in reducing production cost with palladium content below 20%, a sintering temperature below 1050°C, preferably below 1000°C, is necessary, with reduced energy consumption of electric furnace used for sintering. Namely, it is an object of the present invention to provide piezoelectric ceramic compositions having sufficient mechanical strength and excellent piezoelectric properties, suitable for extremely small and thin devices. It is also an object of the present invention to provide piezoelectric ceramic compositions that can be sintered at relatively low temperature.

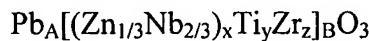
[0004]

Means for solving the problems

The present invention is based on a discovery that in an oxide composition of basic composition formula $Pb_A[(Zn_{1/3}Nb_{2/3})_xTi_yZr_z]_B O_3$, if the Pb atomic ratio is in a certain range below 1 or the Pb atomic ratio is below 1 with addition of a certain amount of at least one oxide chosen from Ta_2O_5 , Sb_2O_3 and Nb_2O_5 , sintering is possible at relatively low temperature and piezoelectric performance and mechanical strength can be improved. Namely, the present invention achieving such objectives concerns piezoelectric ceramic composition comprising oxide composition of basic composition formula:



[In the formula, A, B, x, y and z are atomic ratios satisfying the following conditions: $0.96 \leq A/B < 1$; $x + y + z = 1$; $0.05 \leq x \leq 0.40$; $0.1 \leq y \leq 0.5$; $0.2 \leq z \leq 0.6$]. Furthermore, the present invention also concerns piezoelectric ceramic composition comprising oxide composition of basic composition formula:



[In the formula, A, B, x, y and z are atomic ratios satisfying the following conditions: $0.96 \leq A/B < 1$; $x + y + z = 1$; $0.05 \leq x \leq 0.40$; $0.1 \leq y \leq 0.5$; $0.2 \leq z \leq 0.6$] with addition of more than 0.2 wt% but less than 1.0 wt% of at least one oxide chosen from Ta_2O_5 , Sb_2O_3 and Nb_2O_5 .

[0005]

Practical embodiments of the invention

With oxide compositions $Pb_A[(Zn_{1/3}Nb_{2/3})_xTi_yZr_z]_B O_3$ with composition ratios satisfying

$0.96 \leq A/B < 1$ and $x + y + z = 1$ (with $0.05 \leq x \leq 0.40$; $0.1 \leq y \leq 0.5$; $0.2 \leq z \leq 0.6$), piezoelectric ceramic compositions display high dielectric constant and electromechanical bonding coefficient even at relatively low sintering temperature. With the composition ratio A/B below 0.96, dielectric constant and electromechanical bonding coefficient are small. The composition ratio x of $(Zn_{1/3}Bn_{2/3})$ increases with increasing dielectric constant, but mass production is not done, due to high cost of Nb raw material. If x is smaller than 0.05, dielectric constant and electromechanical bonding coefficient are low, thus needed piezoelectric characteristics cannot be obtained. The Ti composition ratio y and Zr composition ratio z affect the dielectric constant and electromechanical bonding coefficient greatly, and close to the morphotropic phase boundary is especially preferred. Thus, preferred in the present invention for the composition ratios x , y and z are $0.05 \leq x \leq 0.40$, $0.1 \leq y \leq 0.5$ and $0.2 \leq z \leq 0.6$ (provided that $x + y + z = 1$).

[0006]

When the oxide composition ratio A/B is $0.9 \leq A/B \leq 1$, for obtaining piezoelectric ceramic compositions that can be sintered at relatively low temperature and have high dielectric constant and electromechanical bonding coefficient and excellent breaking strength, it is preferred to add at least one oxide chosen from Ta_2O_5 , Sb_2O_3 and Nb_2O_5 in a total amount above 0.2 wt% but below 1.00 wt% of the oxide composition. With such oxide addition below 0.2 wt%, effects of the addition are not displayed sufficiently, while above 1.0 wt%, sintering at low temperature is not possible, resulting in that the insufficient sintering and dielectric constant and electromechanical bonding coefficient and sufficient mechanical strength needed for piezoelectric ceramics cannot be obtained.

[0007]

The piezoelectric ceramic compositions of the present invention can be obtained by the method given below. The starting materials that can be used are PbO, TiO₂, ZrO₂, ZnO and Nb₂O₅ or compounds that can be converted to such oxides by firing (oxide 1); at least one oxide chosen from SrO, BaO and CaO or compounds that can be converted to such oxides by firing (oxide 2); and at least one oxide chosen from Ta₂O₅, Sb₂O₃ and Nb₂O₅ or compounds that can be converted into such oxides (oxide 3). Each oxide is weighed to an amount needed and wet mixed using a ball mill, etc. In the case of adding the oxide 3, it may be added after firing of a mixture of oxide 1 and oxide 2. The slurry medium used in the wet mixing may be water, alcohol such as ethanol, or mixture thereof. After sufficient mixing, the starting materials are fired at about 800-1000°C for about 1-3 h then wet pulverized using a ball mill, etc. Also in the wet pulverization, water, alcohol such as ethanol or their mixture may be used for mixing medium. It is preferred that the wet pulverization is carried out to particle diameter 0.5-2.0 μm. The fired powder obtained by the wet pulverization is dried, and dried powder is mixed with a small amount (about 0.5-8 wt%) of water or binder (e.g., polyvinyl alcohol, etc.) to obtain a paste which is then press-molded under a pressure of about 98-392 MPa (1-4 tons/cm²) by extrusion molding or other molding process. The molded product is then sintered at about 960-1200°C for about 2-5 h to obtain a piezoelectric ceramic product. The sintering may be carried out in air, in an atmosphere having an oxygen partial pressure higher than air or in pure oxygen.

[0008]

Next, the present invention is explained in further detail with examples.

Application Examples 1-4, Comparative Example 1

PbO, TiO₂, ZrO₂, ZnO and Nb₂O₅ were mixed in metal element molar ratios given in Table 1, followed by addition of water to slurry concentration 40-50%, wet mixing using a ball mill for 5 h, firing at 900°C for 2 h, addition of water to the fired product to slurry concentration 40-50%, wet pulverization using a ball mill for 15 h, drying of the resulting slurry, addition of 6 wt% of water, uniaxial press molding under a pressure of 39.2 MPa (400 kgf/cm²) then cold static water pressure molding under a pressure of 392 MPa (4 tons/cm²) to obtain 20 mm angular column then sintering the angular column in air for 2 h at temperature given in Table 1 to obtain piezoelectric ceramics. The piezoelectric ceramics thus obtained were sliced, lapped and diced to obtain angular columns of 1.2 mm x 1.2 mm x 5.0 mm. Either ends of the angular column were printed with silver paste, fired at 700°C and subjected to polarization treatment in a silicone oil at 150°C. The samples thus obtained were allowed to stand for 24 h and measured for k33, ϵ_3^d (1 kHz) and d33 according to EMAS-6100 using Impedance Analyzer HP4194A (product of Hewlett-Packard Co.) Measurement results are given in Table 1. Separately, the piezoelectric ceramics obtained above were sliced, lapped and diced to obtain samples of 2 mm x 4 mm x 0.6 mm (thickness) and the breaking strength was measured according to JIS (R1601) using a digital load tester. The support point distance and loading speed were 2.0 mm and 0.5 mm/min, respectively. The results obtained are given in Table 1.

Application Examples 5-13, Comparative Examples 2-7

Samples were obtained similarly to Application Examples 1-4 by mixing PbO, TiO₂, ZrO₂, ZnO and Nb₂O₅ in metal element molar ratios given in Table 2 with addition of compounds chosen from Ta₂O₅, Sb₂O₃ and Nb₂O₅ in amounts shown in Table 2. Measurements were made for the samples similarly to Application Examples 1-4. Results obtained are given in Table 2.

Application Examples 14-17

The compound PbO was mixed with Pb element molar ratio smaller than 1 as shown in Table 3 with addition of Ta₂O₅ in an amount shown in Table 3, following the procedure of Application Examples 1-4 to obtain samples. Measurements were made for the samples obtained similarly to Application Examples 1-4. Results are given in Table 3. Use of Sb₂O₃ or Nb₂O₅ in place of Ta₂O₅ gave similar results as Ta₂O₅.

[0009]

Effects of the invention

The piezoelectric ceramics of the present invention are excellent in piezoelectric properties and breaking resistance, can be sintered at a temperature below 1000°C, enabling use of inexpensive Ag/Pd = 80/20 as inner electrodes in making laminated piezoelectric devices. Thus, these ceramics are useful for actuators, sound generators, especially useful as laminated piezoelectric device materials.

Table 1

	Pb mol	ZnNb mol	Ti mol	Zr mol	添加剂 wt%	焼成温度 ℃	ρ g/cm ³	k ₃₃ %	c ₃₁ 10 ⁻¹² C/N	ε ₃₃ %	抗折強度 MPa	機械的 強度の 評価	低 温 燒 結 の 評 価
実施例 1	0.99	0.1	0.43	0.47	無添加	1060	7.81	73.0	2048	438	93	○	○
実施例 2	0.98	0.1	0.43	0.47	無添加	1060	7.78	70.9	2047	411	95	○	○
実施例 3	0.97	0.1	0.43	0.47	無添加	1060	7.76	68.2	1904	365	95	○	○
実施例 4	0.96	0.1	0.43	0.47	無添加	1060	7.74	66.7	1732	326	118	○	○
比較例 1	1	0.1	0.43	0.47	無添加	1200	7.87	66.7	1468	318	68	—	—
						1060	7.65	63.6	1406	303	80		

Key: 1 Additive

2 Firing temperature

3 Breaking strength

4 Evaluation of mechanical strength

5 Evaluation of low-temperature sintering

6 Application Example

7 None

8 Comparative Example

Table 2

	Pb	ZnNb	Tl	Zr	試験物	焼成温度	ρ g/cm ³	k33	σ_T	d33	折衝強度 $\times 10^{-11}$ CN	機械的 強度の評価 MPa	低 温 度 の評価 の評価
6 実施例5	1	0.1	0.43	0.47	0.4 Ta205	1000 960	7.97 7.94	73.4 70.0	1634 1453	380 331	95 117	○	○
実施例6	1	0.1	0.43	0.47	0.6 Ta205	1000 960	7.97 7.88	73.0 71.4	1654 1468	377 318	104 114	○	○
実施例7	1	0.1	0.43	0.47	1.0 Ta205	1060 1000 1200	7.89 7.85 7.88	71.4 71.6 73.1	1595 1465 1419	353 333 376	92 101 97	○	○
比較例2	1	0.1	0.43	0.47	0.2 Ta205	1200 1060 1200	7.45 7.45 7.99	74.7 74.2 69.5	1472 1472 1470	376 376 388	112 121	○	×
比較例3	1	0.1	0.43	0.47	2.0 Ta205	1060	6.19	74.4	1474	376	95	○	×
6 実施例8	1	0.1	0.43	0.47	0.4 Nb205	1000 960	7.94 7.82	72.7 70.8	1652 1419	376 337	105 116	○	○
実施例9	1	0.1	0.43	0.47	0.6 Nb205	1060 1000 1200	7.92 7.75 7.86	72.7 69.3 74.2	1571 1627 1555	401 359 471	105 112 90	○	○
実施例10	1	0.1	0.43	0.47	1.0 Nb205	1000 1060 1200	7.88 7.72 7.86	70.6 68.4 74.2	1652 1412 1555	355 318 471	102 109 90	○	○
比較例4	1	0.1	0.43	0.47	0.2 Nb205	1060 1200	7.40 7.89	74.7 65.7	1474 1470	376 348	105 128	○	×
比較例5	1	0.1	0.43	0.47	2.0 Nb205	1060	6.10	74.4	1474	376	95	○	×
6 実施例11	1	0.1	0.43	0.47	0.4 Sb203	1000 960	7.95 7.91	72.6 70.2	1565 1441	361 330	98 107	○	○
実施例12	1	0.1	0.43	0.47	0.6 Sb203	1060 1000	7.93 7.73	73.0 70.1	1611 1403	375 329	109 114	○	○
実施例13	1	0.1	0.43	0.47	1.0 Sb203	1060 1000 1200	7.89 7.73 7.95	70.9 68.2 73.1	1408 1312 1563	329 306 370	104 110 94	○	○
比較例6	1	0.1	0.43	0.47	0.2 Sb203	1060 1200	7.45 7.53	74.7 64.0	1474 1473	376 374	105 123	○	×
比較例7	1	0.1	0.43	0.47	2.0 Sb203	1060	6.62	74.4	1474	376	95	○	×

Key: 1 Additive

2 Firing temperature

3 Breaking strength

4 Evaluation of mechanical strength

5 Evaluation of low-temperature sintering

6 Application Example

7 Insufficient

8 Comparative Example

Table 3

	Pb	ZnNb	Tl	Zr	焼結物	焼成温度	ρ s	t ₃₃	t _r	d ₃₃	抗折強度	機械的強度の評価	低温焼結の評価
	mol	mol	mol	mol	wt%	°C	g/cm ³	%		$\times 10^{-3}$ C/N	MPa		
実施例 14	0.99	0.1	0.43	0.47	0.4 Tz2O3	1060	7.85	74.2	2138	440	110	○	○
実施例 15	0.98	0.1	0.43	0.47	0.4 Tz2O3	1060	7.84	71.5	1983	402	116	○	○
実施例 16	0.97	0.1	0.43	0.47	0.4 Tz2O3	1060	7.82	69.3	1860	360	121	○	○
実施例 17	0.96	0.1	0.43	0.47	0.4 Tz2O3	1060	7.77	67.2	1710	330	123	○	○

Evaluation of mechanical strength: mechanical strength > 88 MPa → ○

Evaluation of low-temperature sintering: sintering temperature < 1000°C → ◎

1000 ≤ sintering temperature ≤ 1050°C → ○ < sintering temperature → X

Key: 1 Additive

2 Firing temperature

3 Breaking strength

4 Evaluation of mechanical strength

5 Evaluation of low-temperature sintering

6 Application Example